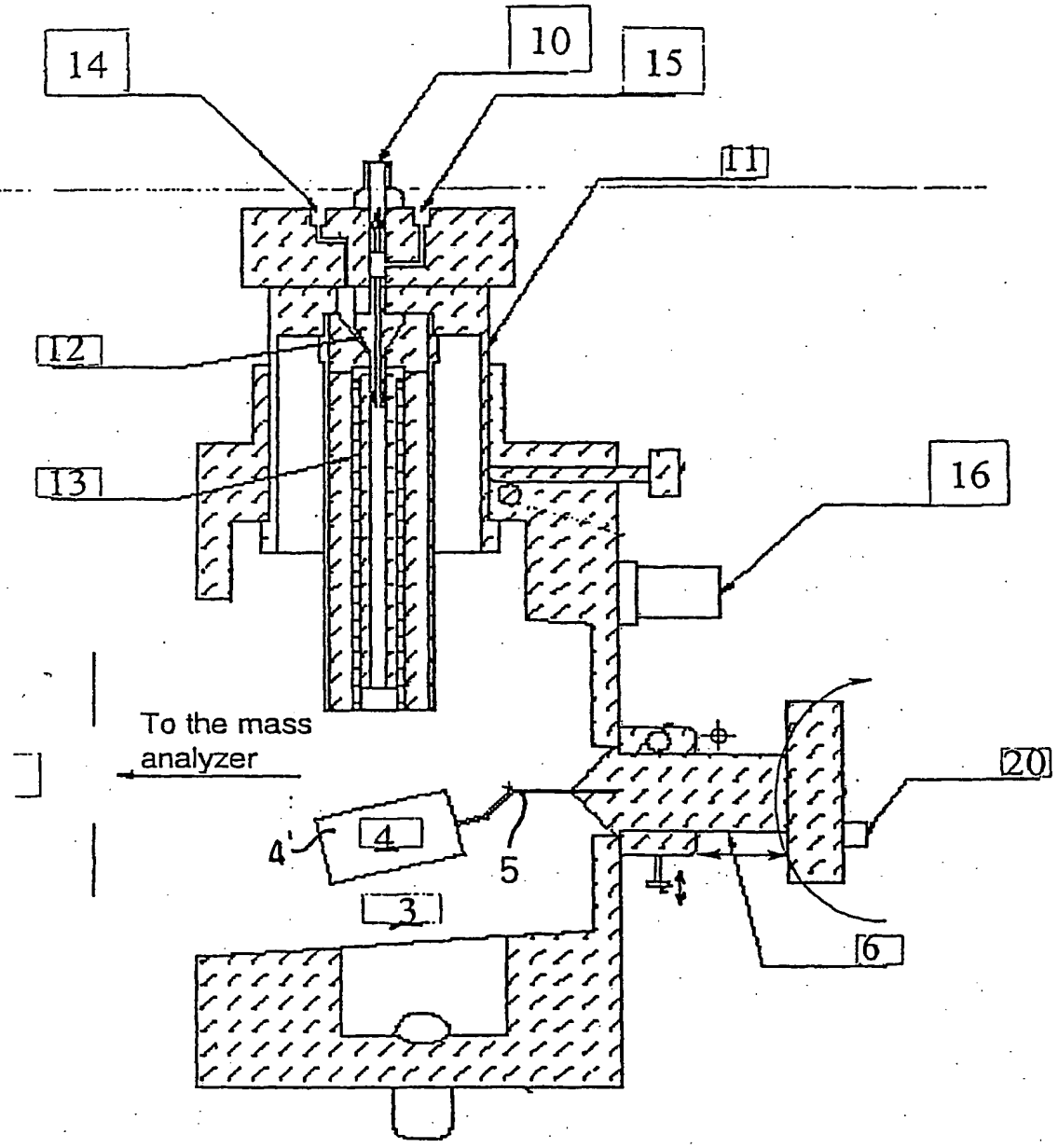

Figure 1

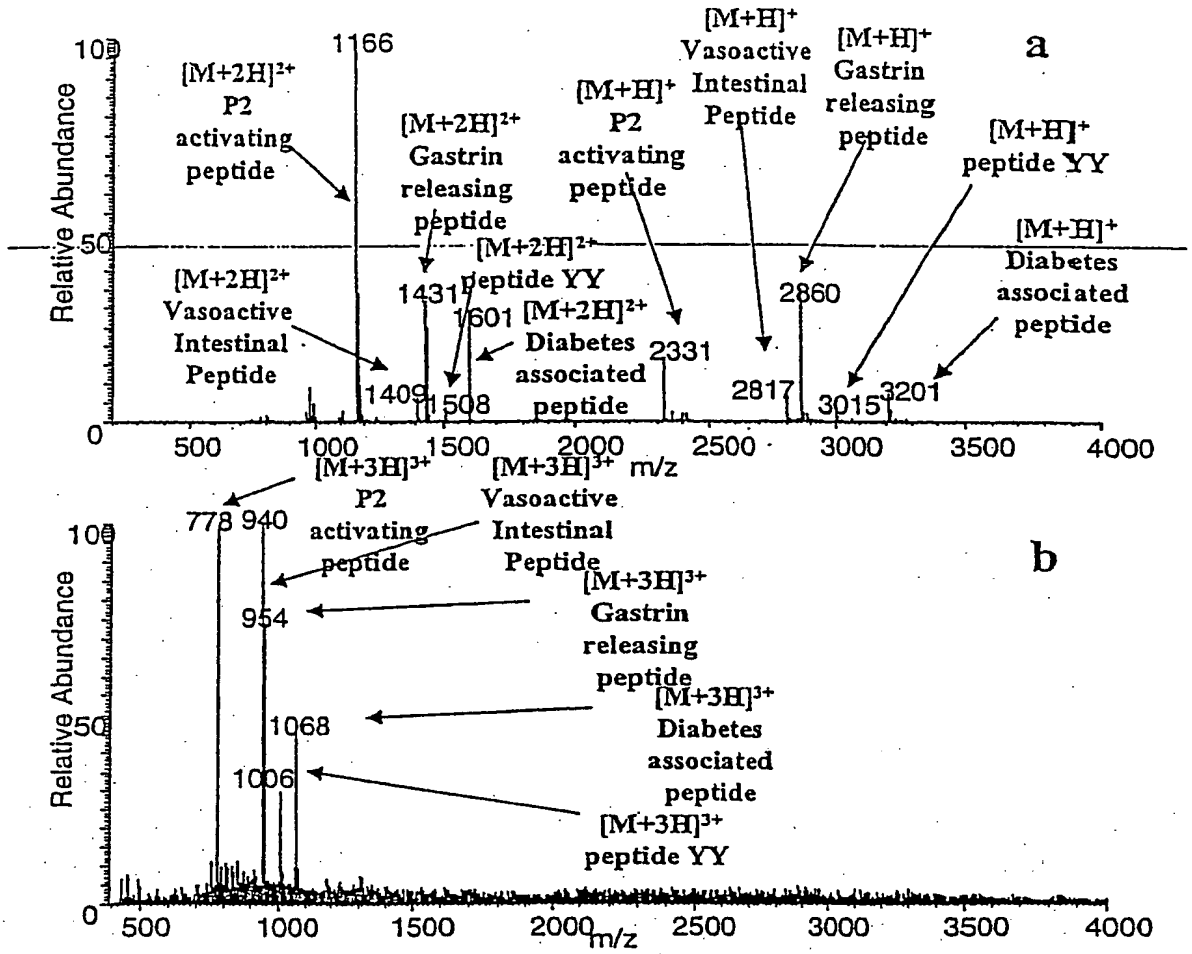

Figure 2: a) Mass spectrum, obtained by direct infusion in the mass spectrometer using the GPSCI technique, of a sample containing a mixture of five peptides (peptide YY fragments 13-36 obtained from Sigma catalog number P6613 MW: 3014 Da; Diabetes associated peptide amine rat fragment 8-37 obtained from Sigma catalog number. D6170 MW:.3200 Da; Gastrin releasing peptide human obtained from Sigma catalog number G8022 MW: 2859 Da; Phospholipase 2 activating peptide obtained from Sigma catalog number. G1153 MW: 2330 Da and Vasoactive Intestinal Peptide Fragment 6-28 obtained from Sigma catalog number V4508 MW: 2816 Da) acquired in the 400 – 4000 Th range. The solution concentration of each peptide was 10-7 M. The counts/s value was 106 and the S/N ratio of the most abundant peak was 500. No salts were added in the pure H2O solution containing the peptides. b) Mass spectrum, obtained by direct infusion in the mass spectrometer using the ESI technique, of the same solution as in (a),. The counts/s value was 105 and the S/N ratio of the most abundant peak was 100

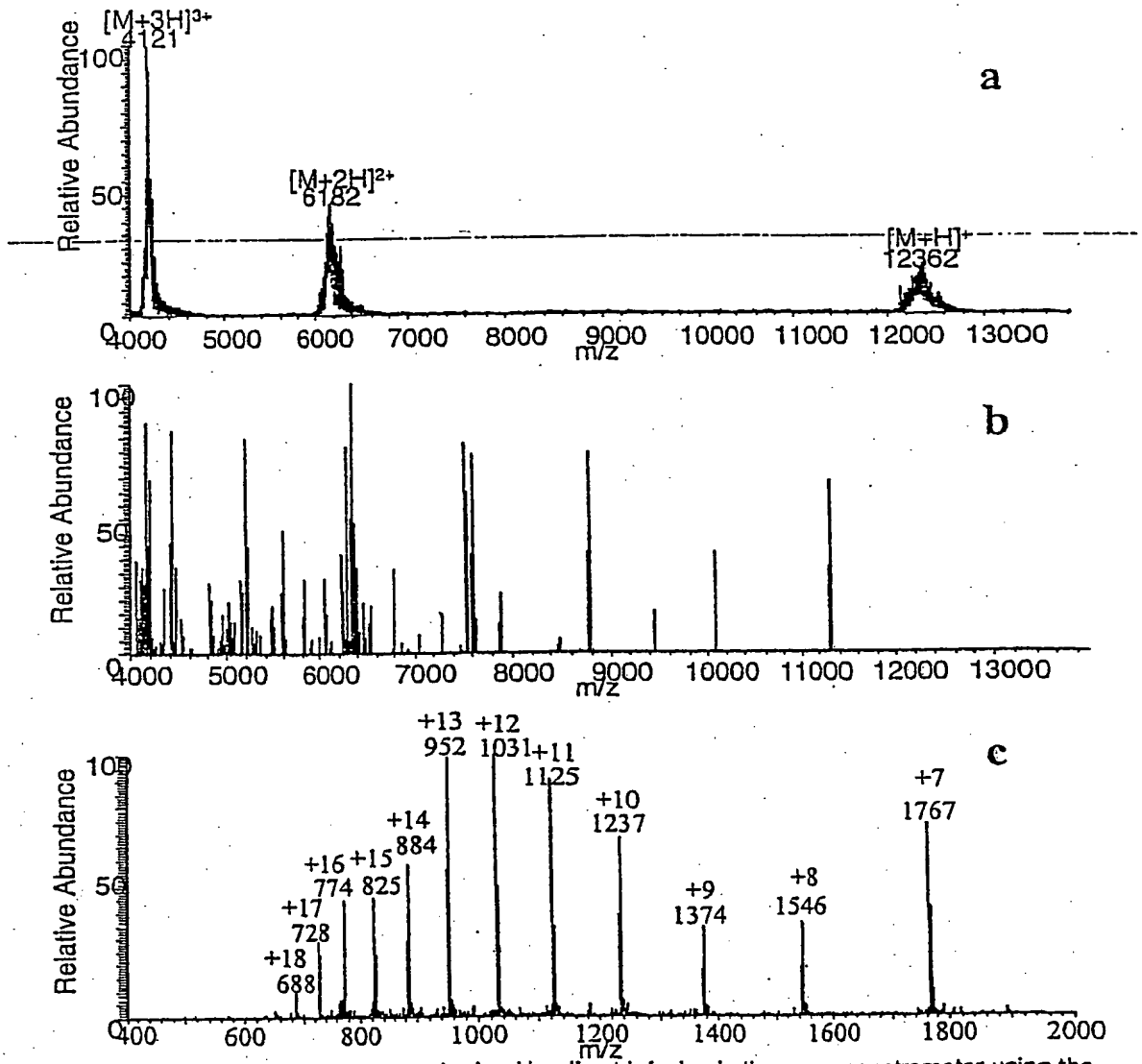

Figure 3: a) Mass spectrum, obtained by direct infusion in the mass spectrometer using the GPSCI technique, of a standard protein (Cytochrome C) acquired in the 4000 – 14000 Th range. The protein was obtained by Sigma-Aldrich (catalog number 10,520-1) and diluted in H2O so to obtain a concentration of 10-7 M. The counts/s value was 106 and the S/N ratio of the most abundant peak was 300. b) Mass spectrum obtained by direct infusion in the mass spectrometer using the ESI technique, of the same solution as in (a). c) Multicharge distribution of the Cytochrome C protein obtained using the ESI ionization source.

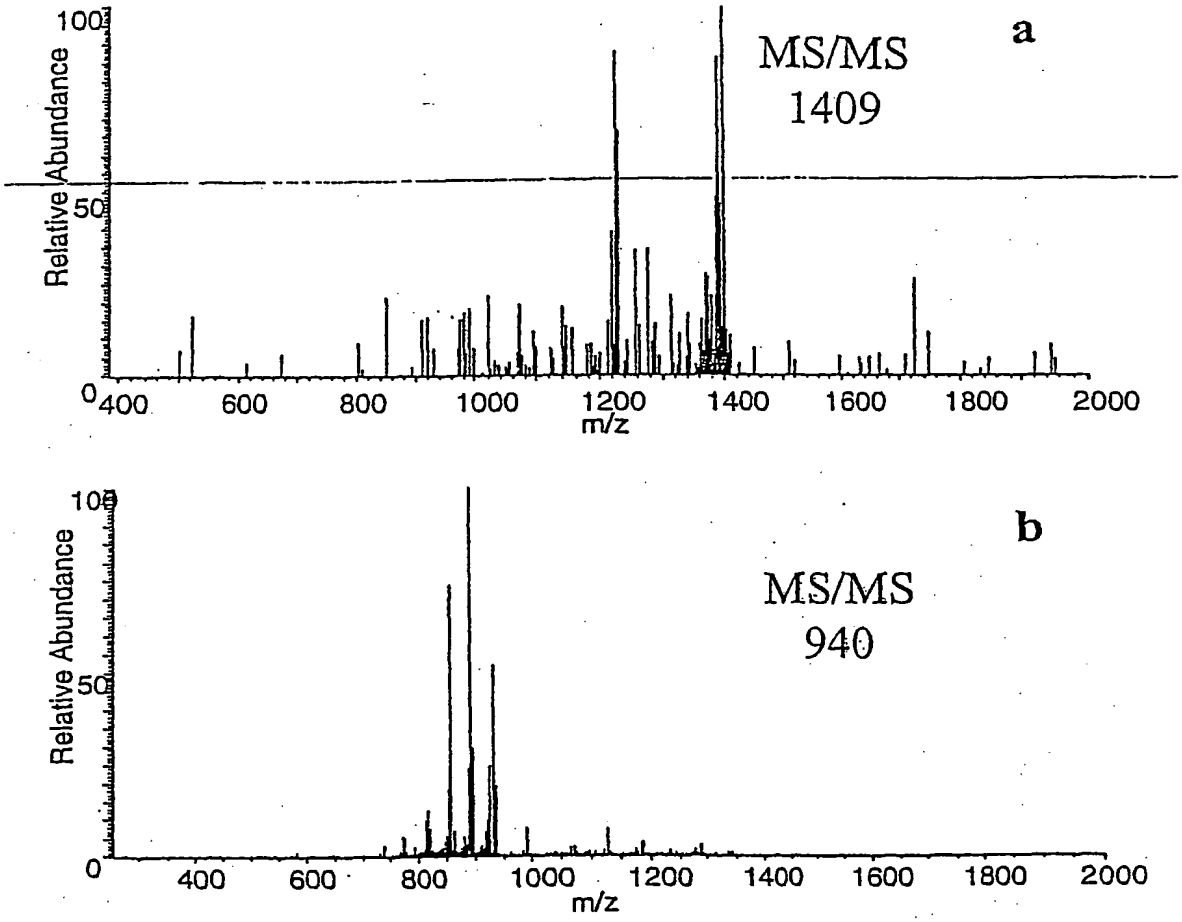

Figure 4: a) Tandem mass spectrum, obtained by using the GPSCI technique, of the bi-charge ion of Vasoactive Intestinal Peptide Fragment 6-28 at m/z 1409. b) Tandem mass spectrum of the same solution, obtained using the ESI techniques. The tri-charge ion at m/z 940 was fragmented.

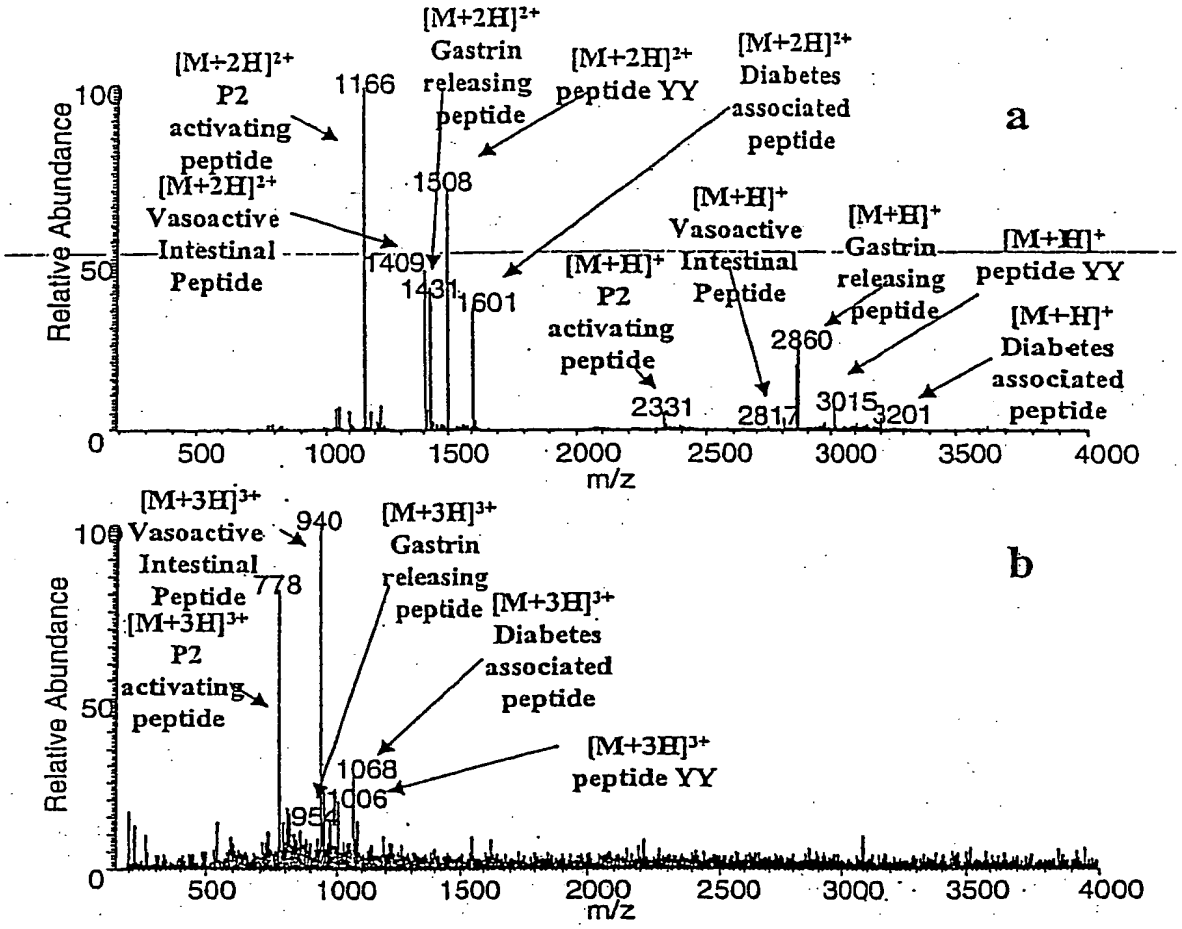

Figure 5: a) Mass spectrum, obtained by direct infusion in the mass spectrometer using the GPSCI technique, of a sample containing a mixture of five peptides, as in figure 2a, acquired in the 400 – 4000 Th range. The solution had a ammonium bicarbonate (NH4HCO3) concentration of 50 mmol/L. The counts/s value was 106 and the S/N ratio of the most abundant peak was 500. b) Mass spectrum obtained by direct infusion in the mass spectrometer using the ESI technique, of the same solution as in (a). The counts/s value was 105 and the S/N ratio of the most abundant peak was 100.

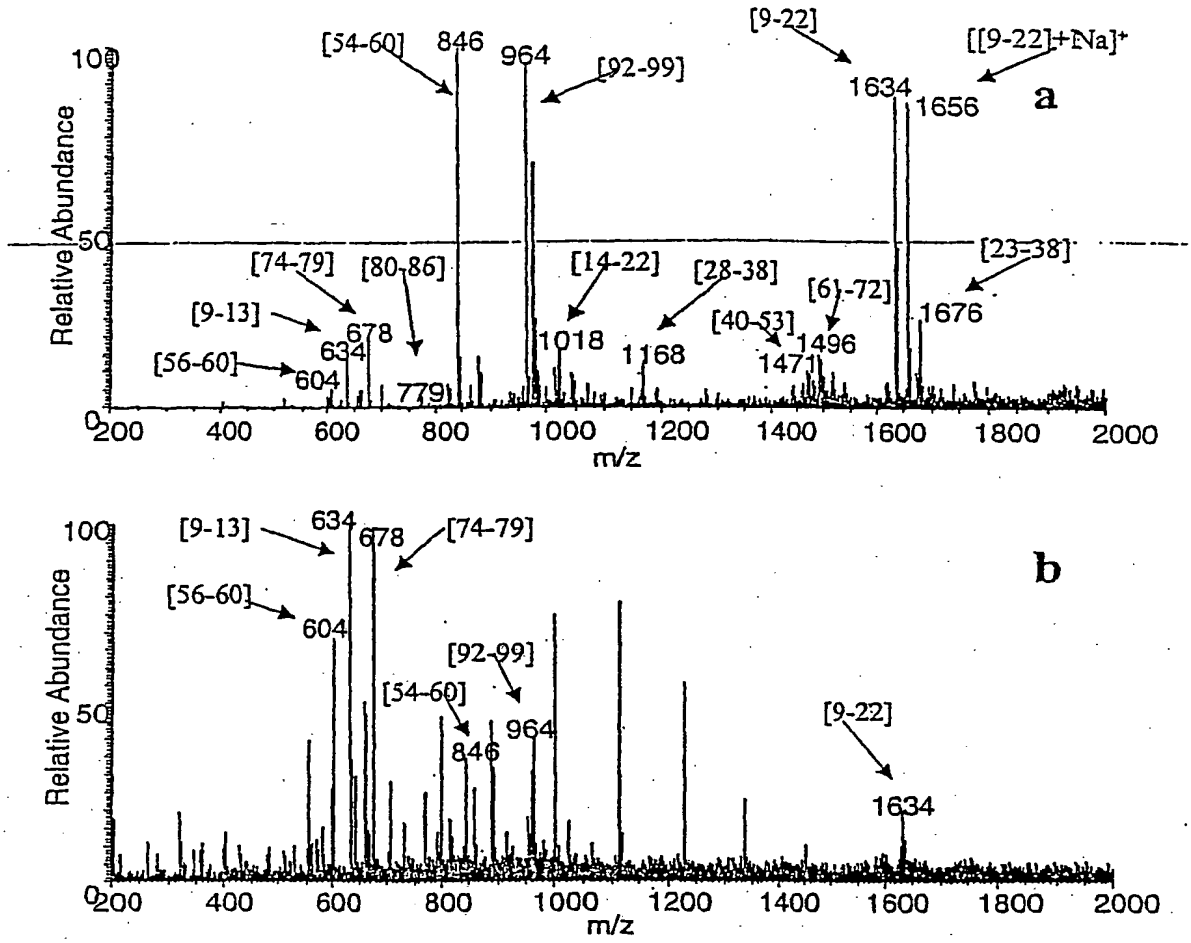

Figure 6: a) Mass spectrum, obtained by direct infusion in the mass spectrometer using the GPSCI technique, of a peptide mixture obtained by tryptic enzymatic digestion of Cytochrome C, in the presence of 50 mmol/L NH_4HCO_3. The identified peptides are marked by their amino acidic intervals as compared with the original protein sequence. The initial (before tryptic digestion) concentration of the protein was 10^{-7} M. The counts/s value was 106 and the S/N ratio of the most abundant peak was 450. b) Mass spectrum, obtained by direct infusion in the mass spectrometer using the ESI technique, of the same solution. The counts/s value was 105 and the S/N ratio of the most abundant peak was 100.

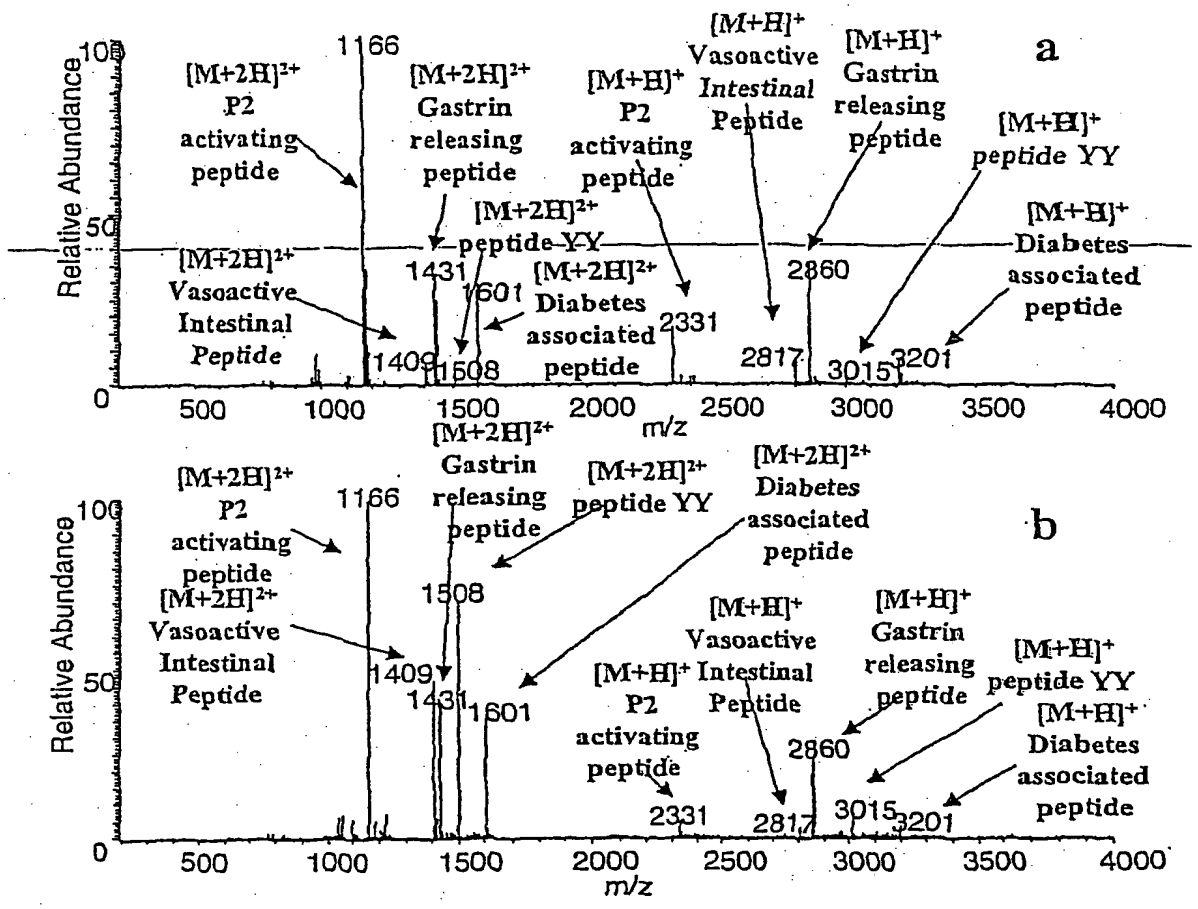

Figure 7: a) Mass spectrum, obtained by direct infusion in the mass spectrometer using the GPSCI technique and in absence of salts, of a sample containing a mixture of five peptides as in Figure 2a. The counts/s value was 106 and the S/N ratio of the most abundant peak was 500. b) Mass spectrum obtained by direct infusion in the mass spectrometer using the GPSCI technique, of a sample containing a mixture of five peptides as in (a), but containing 50 mmol/L NH_4HCO_3.

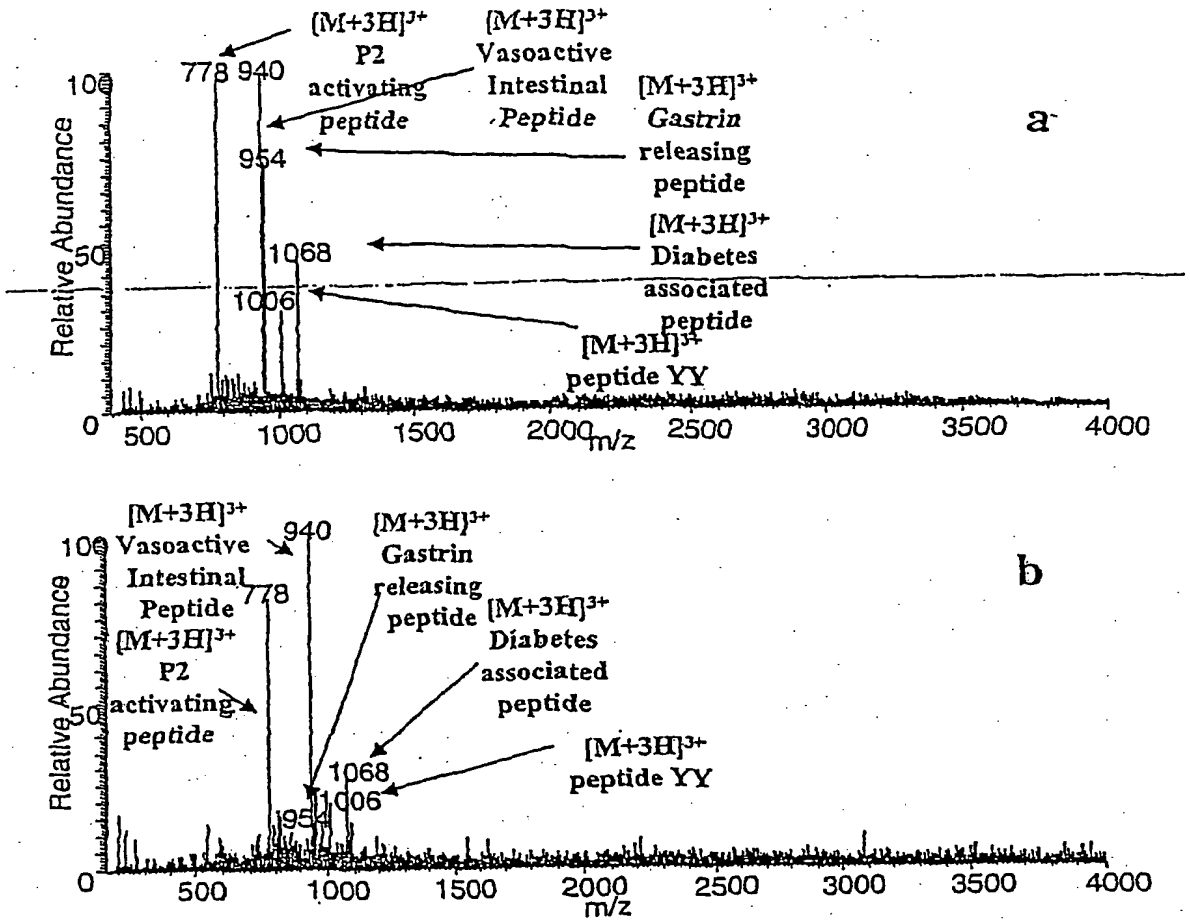

Figure 8: a) Mass spectrum, obtained by direct infusion in the mass spectrometer using the ESI technique, of a sample containing a mixture of five peptides as in figure 2b. The counts/s value was 105 and the S/N ratio of the most abundant peak was 100. b) Mass spectrum, obtained by direct infusion in the mass spectrometer using the ESI technique, of the same sample as in (a) but in the presence of 50 mmol/L NH4HCO3. The counts/s value was 105 and the S/N ratio of the most abundant peak was 100.